



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Yukiko NAKANISHI et al.

Serial No. 09/145,987

Group Art Unit 1745

Filed September 3, 1998

Examiner Mr./Mrs. Leigh MAIER

For: CELLULOSE ACETATE AND DOPE CONTAINING THE SAME

DECLARATION UNDER RULE 132

Honorable Commissioner of Patent and Trademarks,  
Washington, D.C.

Sir

I, Tohru SHIBATA, declare:

That I am a citizen of Japan, residing at 2-1111-290,  
Shiromidai, Himeji-shi, Hyogo, Japan;

That I was born on May 15, 1949 in Shiga;

That I left Graduate Course of the Graduate School  
of Science, the Division of Chemistry II of Hokkaido  
University, JAPAN in 1977 and enrolled in Japan Society  
for the Promotion of Science as a researcher in the  
fellowship program in 1977;

That I received a doctor's degree of Science  
(Hokkaido University) in 1978;

That I enrolled at Department of Chemistry,

University of Wisconsin, USA as a Research Associate in October 1979;

That I have been employed by Daicel Chemical Industries, Ltd., JAPAN since October 1981;

That I appointed as a visiting professor of the Graduate School of Science of Himeji Institute of Technology (current name: University of Hyogo) from 2000 to 2004;

That I carried out development of chiral HPLC columns using cellulose esters from 1981 to 1994, and worked at Specialty Materials & Cellulose Laboratory of Research Center as General Manager from 1994 to 1997;

That I worked at Filter Products Research & Development Laboratory as General Manager from 1997 to 1999, and worked at Research Center as Research Director from 1999 to 2002;

That I have been worked at Cellulose Company, Cellulose R & D of Daicel Chemical Industries, Ltd., as Manager since 2002;

I received the Prize for Chemical Technology from Kinki Chemical Society in 1987, and the Technical Prize from the Society of Fiber Science and Technology in 1988, the Award for Chemical Technology from The Chemical Society of Japan in 1990, and The CSJ Award from The Cellulose Society of Japan in 2005; and

That the following experiments were conducted under

my direct supervision;

### EXPERIMENT

I investigated characteristics of samples corresponding to cited references and the present invention.

#### [Preparation of cellulose acetate]

One-hundred (100) parts by weight of a hardwood kraft pulp ( $\alpha$ -cellulose content 94.5%) was sprayed with 50 parts by weight of glacial acetic acid for activation. Then, a mixture of 470 parts by weight of glacial acetic acid, 265 parts by weight of acetic anhydride, and 8.3 parts by weight of sulfuric acid was added to the activated mixture, and the esterification reaction was carried out in the conventional manner. Thereafter, the hydrolysis reaction was carried out, and magnesium acetate was added as a neutralizing agent to the reaction mixture, and the resulting matter was ripened for about 70 minutes at 60 to 70°C for hydrolysis. After completion of hydrolysis, the resulting dope was discharged in a diluted acetic acid to precipitate a crude product. Thus obtained precipitate was separated from the mixture by dehydration, washed with a purified water, and dried to provide a cellulose triacetate with a degree of acetylation of 60.8% and a viscosity average degree of

polymerization of 320 (CTA, calcium content of 0 ppm and magnesium content of 17.0 ppm ( $0.699 \times 10^{-6}$  mol) per 1 gram).

[Samples A to E]

To calcium hydroxide solutions which have different concentration each other, the flake of the obtained TAC was dipped for treatment. The each CTA flake was filtrated off and dried to produce CTA flake containing the metal contents per 1 gram as shown in Table 1. The content of metal components (calcium and magnesium) contained in 1 gram CTA was measured by an atomic absorption analysis.

[Sample F]

The flake of the obtained TAC (100 gram) was dissolved in a mixed organic solvent of methylene chloride/methanol (9/1 (w/w)) to obtain a solution containing 30% by weight of TAC. Citric acid (6.6 mg, 0.034 mmol) was added to the obtained solution (20 mg citric acid per 1 kg solution).

The amount of the metal component per 100 gram CTA was 0.0644 mmol. The molar ratio of the alkaline earth metal relative to citric acid was 0.49.

The solvent of the dope (solution) was evaporated under a reduced pressure for removal, and a foamed film was obtained. Part of the film was collected, and pulverized under liquid nitrogen to give a sample.

[Flake slurry pH]

The treated flake slurry pH of the samples A to F was determined as follows, and the resulting flake slurry pH value were shown in Table 1.

Weigh exactly 2.0 gram of the sample, previously dried in the form of minute powder, add 80 ml of a boiled distilled water, stir and seal. After standing over night, the mixture was stirred and precipitated. As the sample solution, about 10 ml of supernatant was obtained, and measured pH of the sample solution by means of pH meter corrected. As blank pH, the pH of the boiled distilled water was measured. The hydrogen ion concentration  $[H^+]_s$  and  $[H^+]_b$  (s: sample solution, b: blank solution) of the sample solution and the blank solution were calculated respectively by means of the calculation equation  $[H^+] = 10^{-(pH)}$  (pH represents a pH value measured). In the case of  $[H^+]_s \geq [H^+]_b$ , the slurry pH may be calculated by the following formula:

$$\text{Flake slurry pH} = -\log([H^+]_s - [H^+]_b)$$

In the case of  $[H^+]_s < [H^+]_b$ , the hydroxyl group ion-concentration  $[OH^-]_s$  and  $[OH^-]_b$  of the sample solution and the blank solution are calculated respectively by means of the calculation equation  $[OH^-] = 10^{-14} \div [H^+]$ . The slurry pH may be calculated by the following formula:

$$\text{Flake slurry pH} = 14 + \log([OH^-]_s - [OH^-]_b + 10^{-7})$$

[Stability]

The samples were subjected to hydrolysis for 7 hours in boiled water for evaluating stability of the samples. In each sample, the stability was evaluated based on the amount of generated acetic acid. The results are shown in Table 1.

Table 1

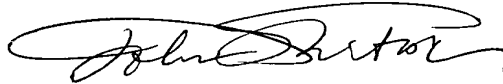
Sample	Flake Slurry pH	Metal content Ion equivalent ( $\times 10^{-6}$ )	Generated acetic acid (%)
A	4.89	4.9	0.028
B	5.15	3.55	0.033
C	4.99	2.67	0.059
D	4.83	2.66	0.095
E	4.26	0.32	0.219
F	4.0	0.32	0.255

#### EVALUATION

As shown in Table 1, samples E and F having a little amount of metal components deteriorates stability including thermal stability and hydrolysis stability. Contrarily, samples A to D have an improved stability.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 19<sup>th</sup> day of August, 2005

A handwritten signature in black ink, appearing to read 'Tohru Shibata', is written over a horizontal line.

Tohru SHIBATA